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Rheology Bulletin

Help with Ringing, Dumbbells, Relaxation Times

Also:

Technical Program Salt Lake City, Utah USA
Notable Passing: Hershel Markovitz
Report on Portland

Creep Ringing in Rheometry *or* How to Deal with Oft-discarded Data in Step Stress Tests!

Randy H. Ewoldt and Gareth H. McKinley
Hatsopoulos Microfluids Laboratory
Department of Mechanical Engineering, MIT
Cambridge, MA 02139

Introduction

Inertial effects are ubiquitous and unavoidable in stress-controlled rheometry. Many readers of this *Bulletin* will have seen the kind of phenomena shown in the experimental data of Figure 1. If the fluid is sufficiently viscoelastic, inertio-elastic 'ringing' events (*i.e.* damped oscillations) are observed in the angular displacement measured at the start of a creep test, as a result of the coupling of instrument inertia and sample elasticity. Even if the fluid is a simple viscous Newtonian fluid one may have noticed that the initial strain response of any real creep test is always quadratic in time, rather than the simple linear response $J(t) = \gamma(t)/\tau_0 = t/\mu$ that is always taught in class. Although well-understood theoretically, effectively dealing with the consequences of inertio-elastic ringing is something with which practitioners of the coarse art of rheometry may not always be comfortable. This note is intended to remind the reader of the sources of these phenomena, and review some methods for extracting useful rheological information from the data rather than simply discarding or deleting them.

Inertial effects are often interpreted as undesirable, because inertia limits the ability to measure the theoretical creep response of an unknown test material at short times. However, effects such as inertio-elastic creep ringing can be exploited in order to rapidly estimate viscoelastic properties. Creep ringing can be deliberately exploited to slightly extend the accessible range of oscillatory measurements, and the data extracted can also be compared with the viscoelastic material properties measured in forced oscillation tests in order to check for self-consistency.

Review

The analysis of inertio-elastic vibrations arising in viscoelastic materials has been practiced for some time. It was apparently one of the most popular methods of (attempting to) extract viscoelastic moduli, especially for low frequencies and low-loss samples, when it was difficult to measure the phase angle (see, *e.g.*, the opening remarks by Markovitz [1]). The earliest protocols were to perform the test under *free* vibrations; that is, a predetermined force was released, and the system was then allowed to return to equilibrium as it underwent damped vibrations (often referred to as 'free damped vibrations' in the literature). Some early rheometer designs incorporated torsional springs, which would exhibit free (and weakly damped) vibrations even when the sample itself had no elasticity. Instrument elasticity complicated the experimental procedure, as pointed out by Walters [2], who noted that the free vibration technique was generally only useful for extracting a viscosity coefficient. Without the torsional spring, however, the analysis and experiments are less difficult. By measuring the ringing frequency ω_* and the *logarithmic decrement* Δ associated with the ringing (to be defined in detail below), Struick [3] showed that the viscoelastic moduli can be *approximated* for small Δ, negligible instrument elasticity, and negligible sample inertia by the following expressions:

$$\begin{aligned} G' &\approx \frac{I\omega_*^2}{b}\left(1+(\Delta/2\pi)^2\right) \\ G'' &\approx \frac{I\omega_*^2}{b}\left(\frac{\Delta}{\pi}\right) \\ \tan\delta &\approx \frac{\Delta}{\pi}\left(1+(\Delta/2\pi)^2\right) \end{aligned} \qquad (1)$$

where I is the moment of inertia of the system, ω_* is the ringing frequency, and Δ is the logarithmic decrement. This is defined as the natural logarithm of the ratio of two successive peaks, or more generally $\Delta=(1/n)\ln(A_1/A_{n+1})$, where A is the amplitude of the ringing above the equilibrium displacement and n is the number of cycles between peaks.

In these expressions, b is a geometry factor given by $\gamma/\tau = b\phi/\Gamma$ that relates the raw (or measured) angular displacement ϕ and torque Γ to the rheological quantities of interest, *i.e.* the strain γ and stress τ (hence $b = F_\gamma/F_\tau$ where $\tau = F_\tau\Gamma$ and $\gamma = F_\gamma\phi$). For example, the geometry factor for a cone-plate is $b_{c\text{-}p} = 2\pi R^3/(3\tan\theta)$, and for a plate-plate, $b_{p\text{-}p} = \pi R^4/2h$. Struick also gives higher order correction

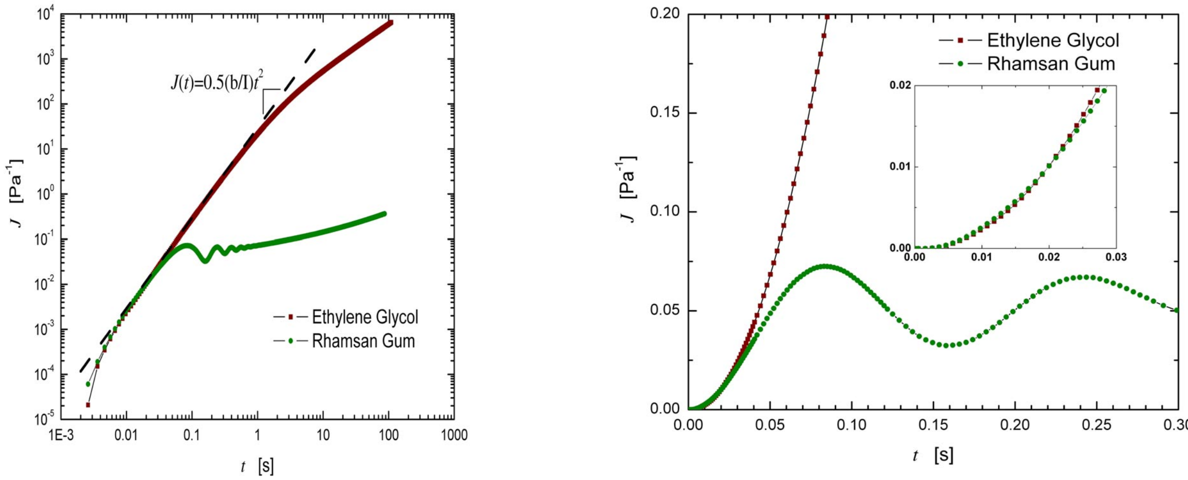

Figure 1: The transient creep response of a viscous Newtonian fluid and a viscoelastic polymeric gel with equivalent instrument inertia and geometry. The viscoelastic fluid exhibits underdamped oscillations but little flow at long times as shown in Figure 1(a). The short time creep response, shown in Figure 1(b), is identical for the two fluids and is completely determined by instrument inertia and geometry. A short time asymptotic solution proportional to t^2 is also shown by the broken line. Creep ringing is caused by the coupling of instrument inertia with the elasticity of the viscoelastic sample (Rhamsan gum (courtesy of CPKelco, San Diego, CA) at 0.75 wt% 250mM NaCl, AR-G2, D=6 cm 2° cone, T=25°C, τ_0=1 Pa for each).

terms to the approximation given above. These corrections are proportional to Δ, ω_*, and derivatives with respect to frequency (to access a range of frequencies, one would need to vary the instrument inertia). Struick also presents a plot of maximum relative error versus logarithmic decrement. For example, at Δ = 1.0 (or equivalently tan $\delta \approx 0.33$ from eq. (1)) the maximum relative error for the elastic modulus is 7%, and for the loss modulus it is 23%. These ideas are also reviewed in the treatise by Ferry [4].

Forced oscillations with precise harmonic control and measurements over many orders of magnitude in frequency are now readily provided by commercial rheometers, and therefore the free vibration technique is no longer a common method of measuring viscoelastic moduli. However, the ringing caused by the coupling of instrument inertia and sample elasticity is still part of the everyday lives of experimental rheologists. Zölzer & Eicke [5] used creep data obtained on a modern controlled-stress instrument to revisit the early ideas of ringing under step-stress loadings, and used the approximations developed for free vibrations to interpret their data; however, this work is not widely known or cited. Another option for obtaining estimates of viscoelastic moduli from observations of free ringing is to assume a specific rheological constitutive model for the material. The differential equation governing the evolution in the sample stress is then coupled with the differential equation of motion for the system, and the resulting time-dependent response can then be solved analytically (or numerically) and regressed to the experimental measurements in order to obtain best-fit material parameters. The resulting equation of motion is of the general form:

$$\frac{I}{b}\ddot{\gamma} = H(t)\tau_0 - \tau_s(t) \qquad (2)$$

where $I = I_{\text{geometry}} + I_{\text{rheometer}}$, $H(t)$ is the Heaviside step function characterizing the imposition of the instrument stress, and $\tau_s(t)$ is the shear stress in the sample arising from deformation. It is immediately apparent that the sample stress is *not* a step function, $\tau_s(t) \neq H(t)\tau_0$, due to the finite inertia of any real rheometric instrument, although it eventually reaches the constant, desired value after the inertial transient has decayed. The constitutive equation for sample stress is coupled with this equation of motion, and the full system of (differential) equations must be solved simultaneously. Arigo & McKinley [6] presented numerical solutions for a four-mode upper-convected Maxwell model in parallel with a solvent viscosity, along with the analytical solution for the single-mode formulation (a convected Jeffreys model). Additional rheological models were considered by Baravian & Quemada [7], including the Kelvin-Voigt and Maxwell models. Baravian & Quemada noted that creep ringing was advantageous in extending the accessible frequency range in measurements on biopolymer gels (they reported ringing at up to 75 Hz) since inertial effects limited the frequency range accessible by forced oscillations.

Illustrative Examples

We turn now to some examples of creep ringing behavior. Figure 2 shows the creep response for three common rheological models: Newtonian, Kelvin-Voigt, and Jeffreys. For each model the ideal creep response is shown (with $I = 0$ in eq. (2)) alongside the actual response that arises due to a finite moment of inertia. For completeness, the analytical solutions for the Kelvin-Voigt and Jeffreys models are given in Table 1 (see e.g. [7] for detailed development of solutions). The Kelvin-Voigt model contains two parameters (a spring of modulus G_K in parallel with a dashpot η_K) and is the canonical model for a viscoelastic solid because it attains a finite strain at

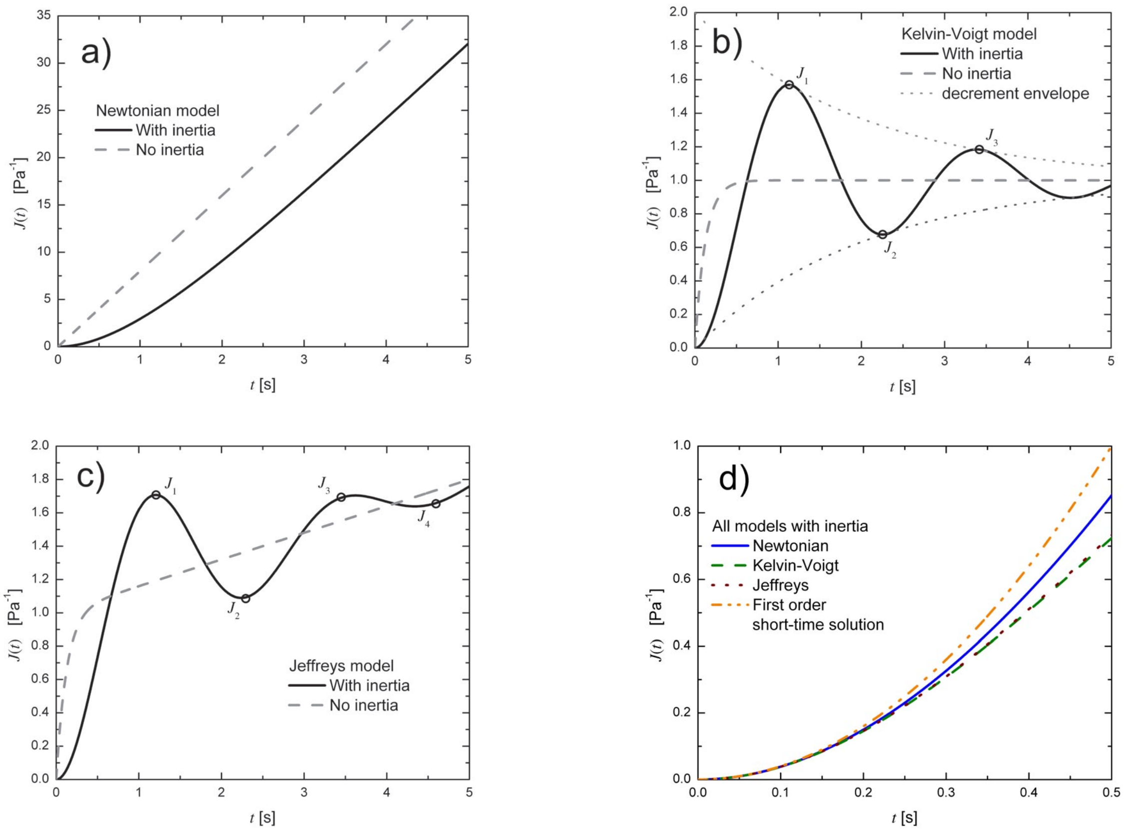

Figure 2: Typical data (simulated) for inertial creep responses compared to ideal non-inertial responses: a) Newtonian; b) Kelvin-Voigt viscoelastic solid, under-damped; c) Jeffreys viscoelastic fluid, under-damped; d) an enlargement of the response near the origin shows that all models have the same quadratic response at short times, which is determined purely by the instrument inertia and geometry factor.

steady state. The Jeffreys model contains three-parameters (one spring and two dashpots), and at steady state shows a steady rate of creep as expected in a viscoelastic fluid. The three elements of the Jeffreys model can be arranged as either a Kelvin-Voigt unit in series with a dashpot, or equivalently as a Maxwell unit (i.e. a spring in series with a dashpot) in parallel with a dashpot [8]. In this work we use the former formulation because it is convenient to see how the results reduce to the Kelvin-Voigt model in the limit η_2 approaches infinity. Ringing is only observed in the under-damped case, corresponding to the sample having sufficient elasticity, G_K, G_J > $G_{critical}$, where $G_{critical}$ is given in Table 1 for each model.

The envelope for determining the logarithmic decrement is also shown for the Kelvin-Voigt model in Figure 2(b). For a viscoelastic solid creep response of the approximate form $J(t) \approx Xe^{\frac{\Delta\omega_*}{2\pi}t}\sin(\omega_* t + \psi) + Y$, the logarithmic decrement Δ can be determined from the absolute value of three peaks, J_1, J_2, J_3 (as shown in Figure 2b) by the formula $\Delta = 2\ln((J_1 - J_2) / (J_3 - J_2))$, which eliminates the need to know the offset bias Y. The logarithmic decrement Δ may then be used in conjunction with eq. (1) to approximate the viscoelastic moduli.

It is apparent from Figure 2(c) that the logarithmic decrement may be more difficult to obtain for a viscoelastic *fluid*, since an irreversible flow component is part of the response. For this case an approximate viscoelastic response is of the prototypical form $J(t) \approx Xe^{-\frac{\Delta\omega_*}{2\pi}t}\sin(\omega_* t + \psi) + Y + Zt$. In this case, the logarithmic decrement can be determined from the absolute value of four peak points, J_1, J_2, J_3, J_4 (shown in Figure 2c) without knowledge of Y or Z, by the formula

$$\Delta = 2\ln((J_1 - 2J_2 + J_3) / (-J_2 + 2J_3 - J_4)) \qquad (3)$$

Figure 2(d) is a close-up of the short time responses of each constitutive model presented in Figures 2(a) – (c). This graphically shows that the initial short time response of any model is related only to the inertia of the system and is quadratic in time. This can be readily observed from eq. (2). Provided the sample being probed does not exhibit

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(Ewoldt and McKinley, continued from page 6)

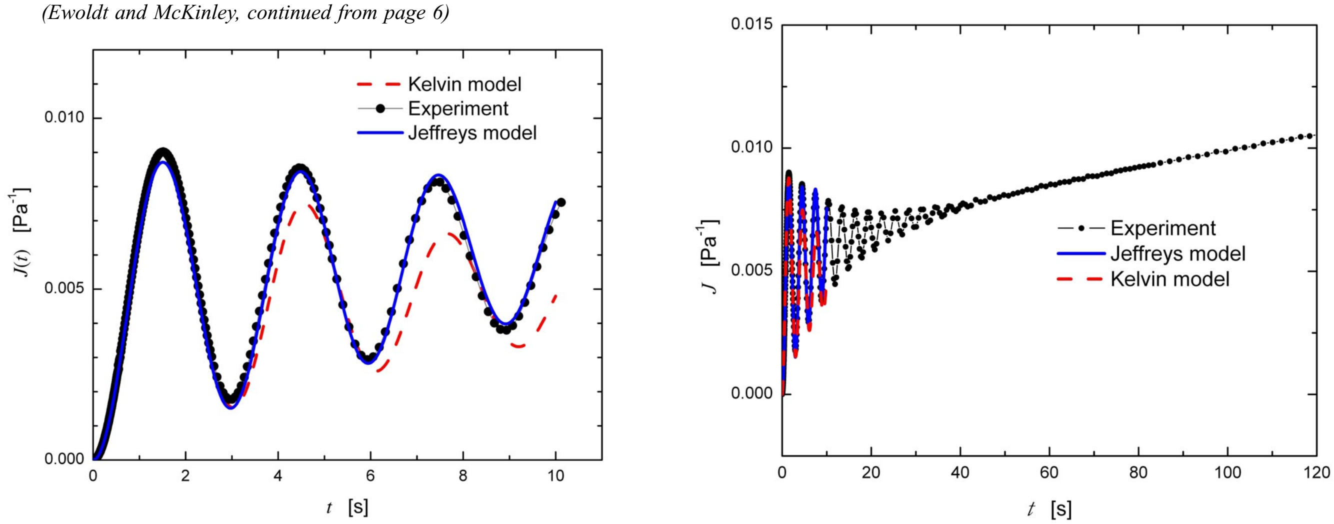


Figure 3: Creep test of native pedal mucus from the terrestrial gastropod *Helix aspera*; inertio-elastic ringing fit to both a Kelvin-Voigt and Jeffreys model (AR-G2, D=0.8 cm plate with sandpaper, 1000μm gap, T=22°C, τ_0 = 5 Pa << τ_y).

any instantaneous (or 'glassy') elastic response, then at time $t = 0^+$ the sample stress resisting the acceleration of the rheometer fixture can be ignored, and the resulting second order differential equation is $(I/b)\ddot{\gamma} = \tau_0$, which can be readily integrated to give $\gamma(t) = \frac{1}{2}(\tau_0 b/I)\, t^2 + \ldots$ for *any* constitutive model. As the shear strain and the shear rate build up in the material, the viscous or viscoelastic stress will retard the acceleration of the fixture. The next order correction to the short time solution is also given in Table 1 for the Kelvin-Voigt and Jeffreys models.

It is clear from the asymptotic expression above that all controlled-stress rheometers undergoing a step-stress loading will exhibit a quadratic response at short times. It is interesting to note that the degree to which this response is actually resolved will vary with the temporal sampling rate of the data acquisition system and the minimum angular displacement (or strain) that can be resolved by the rheometer. As angular resolution and temporal sampling rates increase, inertio-elastic oscillations will become increasingly apparent in short-time creep data.

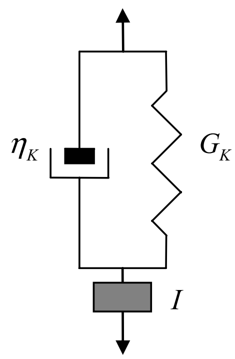
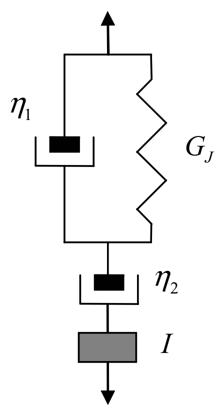
As a further illustration of the creep ringing technique, Figure 3 shows real data from a creep test on pedal mucus (a biopolymer gel) from the terrestrial gastropod *Helix aspera* (also known as the common garden snail). This protein-polysaccharide gel exhibits an apparent yield stress on the order of 100Pa [9] but is dominated by elasticity below the yield stress. The ringing frequency is approximately $\omega_* = 2.14$ rad/s ($f_* = 0.34$ Hz), and the slow decay in the oscillations indicates weak damping. The under-damped oscillatory response for the two-parameter Kelvin-Voigt model and three-parameter Jeffreys model (Table 1) were fitted to the experimental data using a nonlinear fitting routine in MATLAB. Once the model parameters are determined they can be converted into values of G' and G'' (see formulae in Table 1) and compared with the values extracted from the approximate analysis of Struik, which are *model-independent* and use only the ringing frequency ω_* and logarithmic decrement Δ. Here the logarithmic decrement was determined from the first two cycles, using the four-point calculation (Figure 2(c)) to account for the finite flow in the response. Table 2 shows the comparative results, using all three techniques.

The Jeffreys model achieves a satisfying fit to the data especially at short times before any finite flow effects are observed, and will therefore be used as a benchmark for comparing the results. It is interesting that the approximation, based on frequency and logarithmic decrement, does as well or better than the Kelvin-Voigt model at determining the moduli. Here the logarithmic decrement is small ($\Delta \approx 0.25 \ll 2\pi$), which satisfies the low-loss criteria for using the approximation. In addition to achieving a better fit to the data, another benefit of assuming a rheological model is the opportunity to extend the measured result from free oscillations (which are inherently limited to the single frequency, ω_*) to frequencies above and below the ringing frequency. The precision of this extrapolation certainly depends on the quality of the model fit, but at a minimum allows one to estimate the trends in frequency-dependence within a small range of the ringing frequency.

Conclusions

This short note has hopefully clarified some of the key features of inertio-elastic creep oscillations that can often be discerned in the high resolution data obtained with state-of-the-art rheometers. We remind the reader that when the effects of inertia are negligible (at 'long' times $t \gg \{1/A_J, 1/A_K\}$ respectively from Table 1), the frequency-dependent linear viscoelastic moduli can be determined directly from the creep compliance $J(t)$ [4], although the

Table 1: Creep ringing solutions for a Kelvin-Voigt model (viscoelastic solid) and a Jeffreys model (viscoelastic fluid) each coupled with an inertial mass.

Kelvin-Voigt  	for ringing: $G_K > G_{critical} = \frac{\eta_K^2 b}{4I}$ $\gamma(t) = \gamma_K\left\{1 - e^{-A_K t}\left[\cos(\omega_K t) + \frac{A_K}{\omega_K}\sin(\omega_K t)\right]\right\}$ where: $\gamma_K = \frac{\tau_0}{G_K}$ $A_K = \frac{\eta_K b}{2I}$ $\omega_K = \sqrt{\frac{G_K b}{I} - A_K^2}$ with short time response: $\gamma(t) \cong \frac{\tau_0}{I/b}\left[\frac{1}{2}(\delta t)^2 - \frac{1}{6}\frac{\eta}{I/b}(\delta t)^3 + \cdots\right]$ $G' = G_K$ $G'' = \eta_K \omega$ $\lambda_K = \frac{\eta_K}{G_K}$
Jeffreys  	for ringing: $G_J > G_{critical} = A_J^2 \frac{I}{b}(1 + \eta_1/\eta_2)$ $\gamma(t) = \dot{\gamma}_J t - B_J - e^{-A_J t}\left[B_J\cos(\omega_J t) + \frac{A_J}{\omega_J}\left(B_J - \frac{\dot{\gamma}_J}{A_J}\right)\sin(\omega_J t)\right]$ where: $\gamma_J = \frac{\tau_0}{\eta_2}$ $\omega_J = \sqrt{\frac{G_J b}{I}\frac{\eta_2}{(\eta_1 + \eta_2)} - A_J^2}$ $A_J = \frac{G_J + \eta_1\eta_2 b/I}{2(\eta_1 + \eta_2)}$ $B_J = \frac{\tau_0}{G_J}\frac{(\eta_1 + \eta_2)}{\eta_2}\left(\frac{2A_J I}{\eta_2 b} - 1\right)$ with short time response: $\gamma(t) \cong \frac{\tau_0}{I/b}\left[\frac{1}{2}(\delta t)^2 - \frac{1}{6}\frac{1}{I/b}\frac{\eta_1\eta_2}{\eta_1 + \eta_2}(\delta t)^3 + \cdots\right]$ $G' = G_J\frac{(\lambda_2\omega)^2}{1 + (\lambda_1\omega)^2}$ $G'' = G_J\frac{(\lambda_2\omega)\left[1 + (\lambda_1^2 - \lambda_1\lambda_2)\omega^2\right]}{1 + (\lambda_1\omega)^2}$ $\lambda_1 = (\eta_1 + \eta_2)/G_J$ $\lambda_2 = \eta_2/G_J$

Note: see Errata page for corrections

Table 2: Viscoelastic moduli determined from inertio-elastic creep ringing shown in Figure 3 using three different methods: the approximate relation using frequency and logarithmic decrement, and fitting two assumed constitutive models: Kelvin-Voigt and Jeffreys.

	ω_* [rad/s]	G' [Pa]	G'' [Pa]	tan δ
Approximation	2.14	231	18.2	0.08
Kelvin-Voigt	2.03	210	25.9	0.12
Jeffreys	2.11	223	17.0	0.08

frequency range and accuracy will still be limited by the rate of data acquisition and length of measurement. However, the presence of inertia limits the high frequency projection, since the short time response of any real creep test is dominated by inertia, and therefore the sample stress is not actually a step function, $\tau_s \neq H(t)\tau_0$, but instead $\tau_s = H(t)\tau_0 - I\ddot{\gamma}$. The creep compliance is not well defined for these short times. Of course, one way to nearly eliminate instrument inertia is to perform a step *strain* experiment and measure instead the relaxation modulus $G(t)$, in which case it is only the response time of the instrument and sample inertia that become the limiting factors.

As we noted earlier, one reported experimental benefit of inertio-elastic ringing is the ability to achieve higher frequencies than forced oscillations. Note, however, that the ability to resolve this frequency is important, and this depends on the rate of data acquisition of the rheometer. The ringing frequency, to first order, depends on the instrumental parameters and sample elasticity as $\omega_* \sim \sqrt{bG'/I}$. For a given material, the limiting frequency is maximized by increasing $\sqrt{b/I}$. If the inertia of the geometry is much less than the inertia of the instrument, then the choice of geometry should be made to increase b. For a cone-plate $b_{c\text{-}p} \sim R^3/\theta$, where R is the radius and θ is the cone angle, while for a plate-plate $b_{p\text{-}p} \sim R^4/h$, where h is the gap height. Thus, assuming that the total inertia is primarily from the instrument, large diameters with small gaps maximize the ringing frequency by increasing the 'stiffness' of the system. Higher ringing frequencies will also decrease the total timescale of the ringing, since higher frequencies will increase the rate of dissipation in the viscoelastic material (note also in Table 1 that increasing b/I increases the damping rates A_K and A_J, respectively). Decreasing the total ringing time will also improve the approximation of a step-sample-stress, $\tau_s(t) \approx H(t)\tau_0$ (with progressively higher frequency oscillations that are dissipated increasingly rapidly and which can only be observed for short times $t < \{A_J, A_K\}$ respectively). Shifting the ringing frequency to higher values is thus useful for observing creep compliance in viscoelastic materials at shorter timescales.

When analyzing inertio-elastic ringing, the Struik approximation using frequency ω_* and logarithmic decrement Δ can be used as a very rapid manual self-consistency check to compare with forced oscillation tests. If better precision is desired, the higher order terms given by Struick could be used (which require data at multiple frequencies). Alternatively, a rheological constitutive model can be assumed *a priori*, and the ringing response can be fit to this model. At least one commercial software package for rheological analysis includes a routine to fit creep ringing to mechanical models such as those in Table 1 (TA Instruments, New Castle, DE). In this particular software the user is still required to manually convert the fitted model parameters to the viscoelastic moduli $G'(\omega_*)$ and $G''(\omega_*)$. Being aware of the existence of inertio-elastic creep ringing and the quadratic short time response of any material to a step stress loading in a rheometer enables the practicing rheologist to extract useful information from data that is often obscured or ignored.

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The 2006 Student Poster Competition Award was given to Jin Li of the University of Virginia by Poster Session Chair Matthew Liberatore. The award was for his poster "Rheology and Microstructure of Organoclay dispersions," coauthored with Jim Oberhauser.

Errata

1. $\gamma(t) = \dot{\gamma}_J t - B_J + e^{-A_J t}\left[B_J \cos\left(\omega_J t\right) + \frac{A_J}{\omega_J}\left(B_J - \frac{\dot{\gamma}_J}{A_J}\right)\sin\left(\omega_J t\right)\right]$

2. $\dot{\gamma}_J = \frac{\tau_0}{\eta_2}$

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